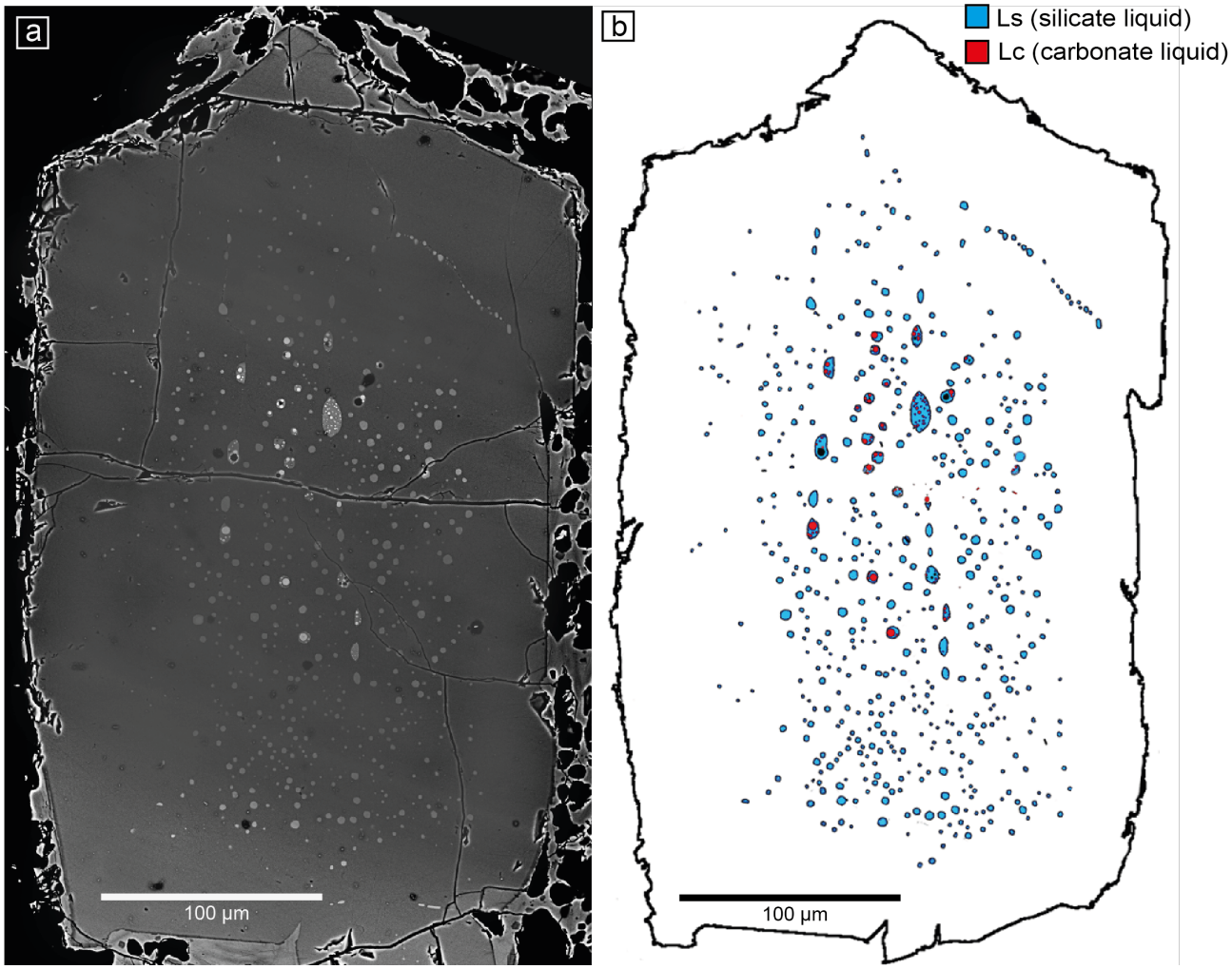
Origin of Carbonatites – Liquid Immiscibility Caught in the Act

Jasper Berndt[1,*] & Stephan Klemme[1]

[1] Institut für Mineralogie, Westfälische Wilhelms-Universität Münster, Corrensstraße 24, 48149 Münster

Email: jberndt@uni-muenster.de, stephan.klemme@uni-muenster.de

*Corresponding author



Supplementary Information Figure 1: Hauyne (a) grain with detected modal % Ls and Lc (b).

BSE image (a) of an exemplary hauyne grain showing melt inclusions containing immiscible silicate (blue) and carbonate (red) liquids (Figure b).

Composition of entrapped phonolite melt parental to Ls and Lc

While phonolites often occur in spatial relations with carbonatites[1,2], the exact composition of the phonolite being parental to Ls and Lc in our study is unclear. According to Liebsch[3] and Schmitt et al.[4] melt from the middle part of the magma chamber, namely layer 1034 from which investigated samples have been collected, represent the potential parental phonolitic melt that has separated to Ls and Lc. However, as shown in Figure 3, the bulk rock composition of layer 1034[5] slightly deviates from the parental melt, mainly in terms of SiO_2, Al_2O_3, and CaO. Thus, the entrapped parental melt must have been a slightly more primitive phonolitic liquid. This is confirmed by a calculated estimation (Lp, Table 1) from the compositions and modal abundances of Ls, Lc, and Ls* indicating that the melt hosting hauyne crystals must have crystallized in less evolved parts of the magma chamber.

Further constraints on liquid immiscibility mechanisms, H_2O and CO_2 concentrations in Lc and Ls, and p-T conditions for carbonatite genesis

Different quenched stages of silicate-carbonate melt separation depending on actual size and shape of the melt inclusions and hence varying thermal gradients during cooling are shown in Figure 2. Assuming the melt inclusions were of similar composition at the time of entrapment and had separated into Ls-Lc liquids before eruption, no such variation in separation stages would occur. More likely, Ls-Lc separation in this part of the magma chamber took place as the LST erupted and the entrapped phonolite liquid fell below the critical solution temperature where the binodal ("solvus") of the silicate-carbonate system was crossed. The melt became unstable and liquid immiscibility took place via binodal demixing/nucleation and growth as indicated by the typical pattern of separate nuclei formation (Figure 2) (e.g.[6,7]). Although cooling must have been quick, probably within seconds to minutes, no spinodal decomposition took place being typical for fast quenched immiscible systems[8]. Thus, liquid immiscibility via binodal demixing/nucleation and growth may be the dominating process for many silicate-carbonate systems as cooling is usually much slower in most geological carbonatite settings, and crossing the metastable region between binodal and spinodal without nucleation is unlikely.

The average analytical total of Lc with C measured is 97.8±2.1 wt% vaguely indicating lower H_2O contents in carbonate liquids compared to Ls where totals indicate H_2O concentrations of about 3.3±1.9 wt% H_2O. However, this is in good agreement with SIMS-determined H_2O contents in LST melt inclusions of 1.5–5.5 wt%[9] and experimentally confined Laacher See phonolite magma water concentrations around 5–6 wt%[10,11]. CO_2 concentrations of LST whole rocks have been determined by Wörner and Schmincke[5] ranging between 100 and 500 ppm which is in overall agreement with Behrens et al.[12] who reported CO_2 solubilities in water-bearing phono-tephritic melt compositions at 200 MPa and 1250°C of 800 ppm at 4 wt% H_2O. Thus, no CO_2, if analyzed, was detected in Ls as the average EPMA CO_2 detection limit in this study was ~ 0.34 wt% (3σ).

Experimental studies reveal that liquid immiscibility is favored at crustal pressures (≤0.1-1GPa[13–15]) due to higher P_{CO_2}[13] while temperatures range from 1250°C for simple analog SiO_2-Na_2O-Al_2O_3-CaO-CO_2 systems[13]

to 700°C for carbonated natural nephelinite[15]. The experimental data agree well with Laacher See magma chamber pressures of ~200 MPa (and less during eruption) at temperatures of ≤760°C[10].

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